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Effect of pH and scale inhibitor concentration on phosphonate–carbonate interaction

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ABSTRACT

In this paper, we present results from five corefloods (RC1 to RC5) from the Jurassic Portlandian limestone (ϕ~19.80% and $k = 606$ mD) using 5000 ppm, 10,000 ppm, 25,000 ppm and 27,000 ppm of partly neutralized Diethylenetriamine pentamethylenephosphoric acid (DETPMP) at pH 4 and 2. The purpose of this study was to study the effect of inhibitor concentration and pH on the inhibitor adsorption and on the evolution of the inhibitor and cation (calcium and magnesium) return concentrations. These corefloods were performed using long cores (12 in.), which were treated with just 0.5 pore volume (PV) of inhibitor. Another purpose was to study the transport and inhibitor/carbonate rock interactions when less than 1 PV of inhibitor solution is injected. This allows for consumption of the inhibitor during propagation and return, rather than saturating the core with many PV to full adsorptive capacity of the inhibitor/rock system. This study showed that the higher the concentration of SI and lower the pH, the more calcium dissolution is observed (from the [Ca^{2+}] effluents). In all treatments there is a decrease in the [Mg^{2+}] effluent corresponding directly to the increase in calcium. The effluent cation results in the long corefloods which strongly support the view that *both* magnesium and calcium are binding quite strongly to the DETPMP scale inhibitor. These observations lead us to a number of conclusions on the factors that must be included in a full carbonate model. In particular, our experimental results, along with some simple modeling, greatly clarify the role of both calcium and magnesium in the mechanism of the scale inhibitor retention in carbonate systems.

1. Introduction

A common problem, in oilfield reservoirs is scale deposition. Scale is an assemblage of deposits that can develop in the formation pores near the wellbore reducing formation porosity and permeability. It can block flow by clogging perforations or forming a thick lining in production tubing (Fig. 1). The build-up of scale inside well bores and the surrounding reservoir causes millions of dollars in damage every year (Mackay et al., 2003). Oilfield scales are inorganic crystalline deposits that form as a result of the precipitation of solids from brines present in the reservoir and production flow system. This scale formation is the result of changes in the ionic composition, pH, pressure and temperature of the brine. Common scales are calcium carbonate ($CaCO_3$) and barium sulphate ($BaSO_4$). When the formation of sulphate or carbonate scale is a problem in producer wells, the most common remedy is to treat the formation with scale inhibitor chemicals in a "squeeze" treatment (Fig. 2) (Crowe et al., 1994; Norris et al., 2001). Phosphonates are one of the most common types of non-polymeric scale inhibitors, which are used commercially in oilfield operations. The phosphonate scale inhibitor Diethylenetriamine pentamethylenephosphoric acid (DETPMP) is known to be amongst the strongest adsorbing scale inhibitor onto carbonate.

Adsorption is often the primary mechanism of SI retention during squeeze treatments of sandstone formations. The scale inhibitor retention mechanism can be more complex than simple adsorption within carbonate reservoirs because the carbonate rock is a much more reactive substrate. In carbonate formations, scale inhibitors are deliberately allowed to react with the formation and precipitate as the slightly soluble calcium salt. This can result in longer scale protection times. Even fully neutralized inhibitors react with carbonates to form precipitates (Crowe et al., 1994).

Reactions that govern the inhibitor squeeze and return are very complicated. Several factors, such as pH, [Ca^{2+}], [Mg^{2+}], temperature, rock mineralogy etc, affect the adsorption level and the shape of the adsorption isotherm (Jordan et al., 1994; Baraka-Lokmane and Sorbie, 2004, 2006).

The Rice University Brine Chemistry Consortium has carried out a large number of studies on the scale inhibitor retention in carbonate-rich formations during squeeze treatments (Kan et al., 1992, 2004a,b, Tomson et al., 2004; Kan et al., 2005). From these "batch" studies, some of their conclusions were:

(1) calcite is the primary solid responsible for phosphonate retention and clay plays a secondary role in phosphonate retention;
(2) although formation mineralogy can be a factor, the primary control of inhibitor retention and return is the pill acidity and concentration; and

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Fig. 1. The build-up of scale inside a tube.

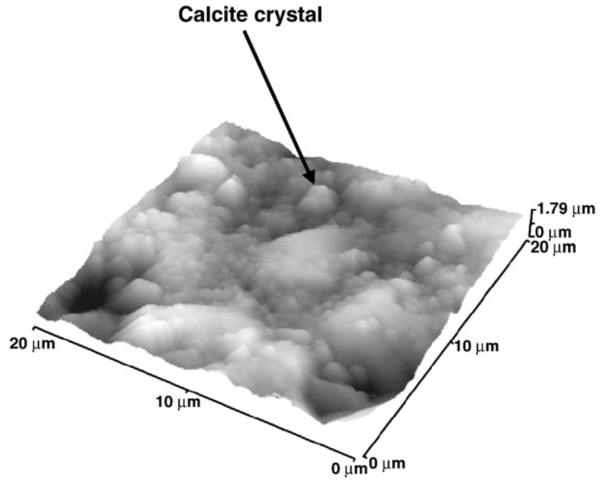

Fig. 3. AFM image of the coreflood RC4 showing the morphology of the rock surface.

(3) salt forms at higher pill concentration. This is due to the calcite surface poisoning that lowers the pH of phosphonate–calcite reaction.

The current study carries over some of this work into the realm of dynamic corefloods and we compare our conclusions with those of the Rice U. group. The purpose of this work is to study the mechanisms and the factors that affect the retention of the phosphonate scale inhibitor DETPMP in carbonate formations. We present coreflooding results using DETPMP to study the effect of inhibitor concentration and pH on inhibitor adsorption and on the behaviour of the inhibitor and cation (calcium and magnesium) concentration. “Contained” corefloods were performed to study the transport and inhibitor/carbonate interactions of the phosphonate inhibitor when less than 1 PV is injected. This allows the analysis of the consumption of the inhibitor during propagation and desorption, rather than saturating the core with many PV of SI solution to reach full adsorptive capacity of the inhibitor/rock system.

2. Mineralogy of carbonate rock material

Carbonate rocks contain more than 50% of the world's hydrocarbon reserves. The carbonate reservoirs have complex pore systems, mainly because they are particularly sensitive to post-depositional diagenesis, including dissolution, dolomitization and fracturing processes. Carbonate mineralogy is usually simple — principal minerals are calcite, dolomite, and minor quantities of clay (Choquette and Pray, 1970; Roehl and Choquette, 1985).

In order to carry out a systematic study in well-characterized carbonate cores, a permeable carbonate rock material has been sourced. Sample material was acquired from the Albion Stone Quarries Ltd, Isle of Portland. This rock originates from the Portland Basebed stone and is an open textured oolitic limestone from the Jurassic Portlandian Formation. The <3.5 m thick Basebed is the lower part of the Freestone series, which comprises the Portland Roach, Portland Whitbed and Portland Basebed Formations and is underlain by a cherty series.

In this study, five methods were used to characterize the rock material: X-ray diffraction (XRD), petrographic thin section, atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). XRD analysis was carried out both on whole rock and on the fine particle fractions. The results of the bulk rock XRD analysis show that the rock material is composed mainly of pure calcite (98 to 99.9%). Quartz constitutes between 2 and ~0.1% of the rock. Analysis of the fines showed that no clay minerals are present. Figs. 3 and 4 characterize the morphology of the rock surface showing the calcite crystals and the shell fragments. The petrography analysis shows that the rock material is a pure porous marine oolitic limestone

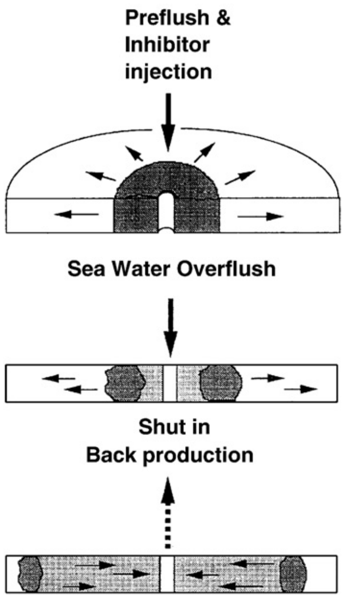

Fig. 2. Squeeze treatment of producer well.

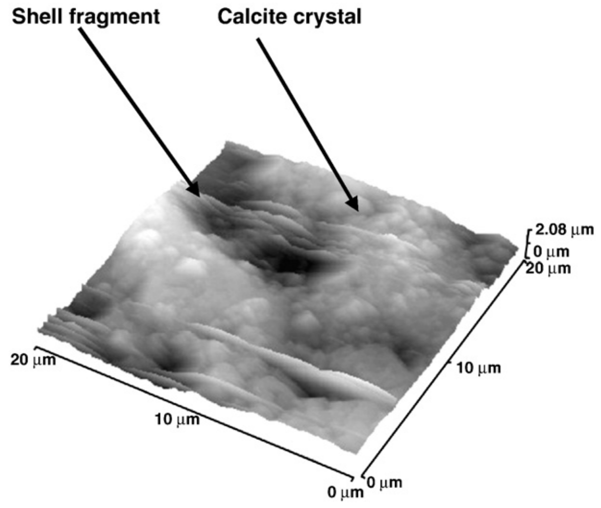

Fig. 4. AFM image of the coreflood RC4 showing the calcite crystals and the shell fragments.